Electrochemical synthesis of metal nanoparticles using a polymeric mediator, whose reduced form is adsorbed (deposited) on an electrode

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Efficient mediated electrosynthesis of nanocomposite Au@*p*(MVCA^{8+}-*co*-St) (~6 nm), in which ultrasmall Au nanoparticles (Au-NP) were bound in nanocapsules of water-soluble nanoparticles of copolymer *p*(MVCA^{8+}-*co*-St) of tetraviologen calix[4]resorcinol (MVCA^{8+}) with styrene (St), was accomplished by the reduction of Au^{I} in aqueous medium. The quantitative reduction of Au^{I} was carried out using the theoretically necessary amount of electricity and was not accompanied by the deposition of metal on the electrode. Radical cations of viologen units MV$^{\bullet+}$ of the molecule *p*(MVCA$^{4\bullet+}$-*co*-St) adsorbed on the electrode and π-dimers MV$^{\bullet+}$···MV$^{\bullet+}$ of π-polymers [*p*(MVCA$^{4\bullet+}$-*co*-St)]$_n$ deposited on the electrode acted as the reducing agents with respect to Au^{I}. During electrolysis, the nanoparticles agglomerated to 37—50 nm. The nanocomposite particles dispersed in ethanol had sizes of 72±16 nm and also contained Au-NP with sizes of 51±8 and 19±3 nm. The catalytic activity of the nanocomposite in the reduction of *p*-nitrophenol with sodium borohydride was demonstrated. A similar reduction of AgCl nanoparticles (~250 nm) led to the formation of silver nanoparticles with crystallite sizes in the range of 7—11 nm, the process was inefficient, however, even when using 250% of electricity, an incomplete reduction of AgCl was still observed.

Key words: electrochemical reduction, mediator, nanocomposite, nanoparticles, gold, silver, polymeric nanocapsule, tetraviologen calix[4]resorcinol.

At the present time, the chemical reduction of metal ions (complexes) using a variety of reducing agents is the most successful and in-demand method of synthesizing metal nanoparticles (M-NP) in bulk solution.[1—7] For a long time, the attention of researchers was attracted by electrochemical reduction (ER) of metal ions to metal, developed in order to obtain metals, metal black, electroplating, refining of metals,[8] and, recently, to obtain M-NP on the surface of electrodes.[9] However, electrosynthesis of M-NP in bulk solution is used quite rarely. This is due to the fact that metal(0) formed during ER of ions is, as a rule, deposited on the electrode. In all the considered cases of obtaining metals (for example, see Ref. 8), their deposition on the electrode is a target process, however, it becomes the main complication for the electrosynthesis of M-NP in bulk solution. A series of approaches to solve this problem have been described. For example, pulse sonoelectrochemistry[10—12] combines the deposition of M-NP on the electrode surface during short-term ER of metal ions with the subsequent transfer of M-NP to the solution by sonication of the electrode. In the works,[13—17] ER of ions was carried out in aprotic organic media using salts of surface-active cations such as tetraalkylammonium or phosphonium as the supporting electrolyte, which prevented the deposition of M-NP. In the case of mediated electrosynthesis,[18—32] the ER of metal ions is relocated from the electrode surface to bulk solution. In this case, the mediator ($M_{ox} \rightarrow M_{red}$) is reduced at the cathode, its reduced form diffuses into bulk solution and reduces the metal ion or complex, which almost completely eliminates metal deposition on the electrode. This method was shown to be efficient for obtaining Pd,[18—22] Ag,[23—27] Co,[28] Au,[29—31] and Pt nanoparticles.[32] The mediators (methylviologen, anthracene, molecular oxygen, fullerene C_{60}) and the media were selected so that neither the mediators, nor their reduced forms would be adsorbed (deposited) on the electrode.

However, a mediated electrosynthesis of M-NP, in which the mediator and/or its reduced form are adsorbed on the electrode, is theoretically possible. So, if M_{ox} is adsorbed, but M_{red} is not adsorbed, then the reduction of metal ions will also occur in bulk solution, and in the

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 0215—0229, February, 2018.

1066-5285/18/6702-0215